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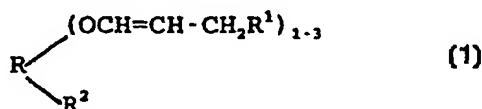
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(54) Title: RADIATION-CURABLE PROPENYL COMPOUNDS, USES THEREOF, AND COMPOSITIONS CONTAINING THEM



(57) Abstract

Disclosed are compounds of formula (1): R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms; R¹ is -H or -CH₃; R² is -OH, alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloxy, methacryloxy, or A-(Het)₀₋₁C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-; or R² is -L-X-(L-R-(OCH=CH-CH₂R¹)_n)₁₋₃ wherein X has any of the structures -Ph₀₋₁-C₆H₄-Ph₀₋₁-Ph₀₋₁-(cyclo-C₅₋₂₀-alkyl)-Ph₀₋₁-, -Ph-Ph-, or -Ph-, wherein Ph is phenylene and a is 1 to 20; -C_fH_{2f}C(O)C_gH_{2g}-, -C_fH_{2f}OC_gH_{2g}-, -C_fH_{2f}C(O)OC_gH_{2g}-, -C_fH_{2f}PhC_gH_{2g}-, or -C_fH_{2f}C(O)NHC_gH_{2g}-, wherein f and g are each 1 to 12; and each L is independently a chemical bond or -C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-, provided that each R is bonded to an oxygen atom of L; or X is -C(O)-, each L is a chemical bond, and i is 1. Also disclosed are methods and compositions useful in the radiation-induced polymerization of such compounds.

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RADIATION-CURABLE PROPENYL COMPOUNDS,
USES THEREOF, AND COMPOSITIONS CONTAINING THEM

1 The present invention relates to novel
radiation-curable propenyl compounds, to radiation-
curable compositions containing such compounds, and to
processes for forming radiation-cured products from
5 such compounds and compositions.

 Radiation curing has become an important and
useful technique for applying and curing coatings,
inks, and adhesives. As described herein, radiation
curing involves presenting a radiation-curable
10 polymer, typically in combination with a photo-
initiator, and exposing the composition to radiation
in the form of ultraviolet or electron-beam radiation
to cause the radiation-curable compound to polymerize.

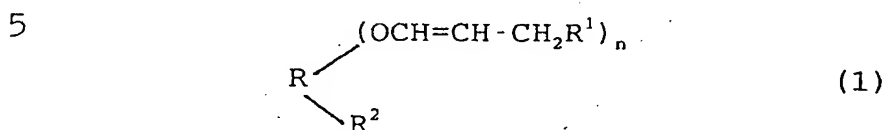
 Radiation curing presents many advantages,
15 such as high rates of throughput, low energy
requirements, and low equipment costs. In addition,
it is advantageous that users are able to avoid using
a solvent when the composition to be radiation-cured
is prepared. Solvents typically would lead to
20 environmental and/or safety hazards, and would require
additional equipment and handling steps to remove the
solvent.

 Propenyl compounds useful in the preparation
of polymeric coatings and the like via
25 photopolymerization are disclosed in, for instance,
U.S. Patent No. 5,486,545 and U.S. Patent No.
5,567,858. However, there remains a need for
radiation-curable compounds, photopolymerizable or
otherwise, which provide improved versatility and
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which can be formulated into a variety of coatings,
 1 films and the like readily and rapidly.

The present invention comprises compounds of
 the formula (1)



wherein n is an integer from 1 to 3;

10 R is linear, branched or cyclic alkyl
 containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

R² is -OH, alkoxy containing 1 to 20 carbon
 atoms which is optionally substituted with phenyl and
 15 two consecutive carbon atoms of which are optionally
 bonded to an oxygen atom to form an epoxy ring,
 phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)_{0.1}-
 C(O)O- wherein A is alkyl containing 1 to 20 carbon
 atoms, and (Het) is -O- or -NH-;

20 or R² is -L-X-(L-R-(OCH=CH-CH₂R¹))₁

wherein X has any of the structures -Ph_{0.1}-C_aH_{2a}-Ph_{0.1}
 -Ph_{0.1}-(cyclo-C₅₋₂₀-alkyl)-Ph_{0.1}-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

-C_fH_{2f}C(O)C_gH_{2g} -C_fH_{2f}OC_gH_{2g}-, -C_fH_{2f}C(O)OC_gH_{2g}-, -C_fH_{2f}PhC_gH_{2g}-,
 25 or -C_fH_{2f}C(O)NHC_gH_{2g}-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

provided that each R is bonded to an oxygen atom of L,

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and i is an integer from 1 to 3; or X is -C(O)-, each
1 L is a chemical bond, and i is 1.

Furthermore, the compounds in formula (1),
can contain up to (n-1) (OCH₂CH=CHR¹) groups in place of
(OCH=CH-CH₂R¹) groups.

5 The present invention is further directed to
compositions comprising one or more compounds of said
formula (1), and also comprising one or more
photoinitiators in an amount effective to mediate
polymerization of said compound when the composition
10 is irradiated with, for instance, ultraviolet
radiation or electron beam radiation.

Still further, the present invention is
directed to a process of forming a polymeric
structure, such as a coating, film, or solid body,
15 comprising forming the aforementioned composition of
one or more compounds of formula (1) and a
photoinitiator, and then irradiating the composition
with ultraviolet or electron beam radiation effective
to polymerize said one or more compounds of formula
20 (1).

Referring to formula (1), it can be seen
that R represents a linear, branched or cyclic alkyl
group having at least two substituents and as many as
four substituents, one of which is a R² group and up
25 to (n) of which have the formula -OCH=CH-CH₂R¹. As
will be described below, up to (n-1) substituents can
have the formula -OCH₂CH=CHR¹ instead of -OCH=CHCHR¹.
Preferred R groups include the branched structures
having the formula CH₃C(CH₂-)₃, or C(CH₂-)₄.

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Referring again to formula (1), it can be
1 seen that the R^2 substituent always contains an oxygen
atom which is also bonded to the R group. Thus, R^2
can be hydroxyl, in which case the resulting compound
is referred to herein as "underivatized".
5 Alternatively, R^2 can be alkoxy containing 1 to 20
carbon atoms, phenoxy, acryloyloxy, methacryloyloxy,
or any of the acyloxy, acyloxycarbonyloxy, or urethane
derivatives represented by the formula $A-(Het)_{0-1}-$
C(O)O- wherein A is alkyl containing 1 to 20 carbon
10 atoms, and (Het) represents the optional oxygen or NH-
atoms. When R^2 is alkoxy it can optionally be
substituted with phenyl, thereby creating for example
a benzyloxy substituent. When R^2 is alkoxy containing
two or more carbon atoms, two consecutive carbon atoms
15 thereof can optionally be joined with an oxygen atom
to form an epoxy ring. The embodiments wherein R^2 is
other than hydroxyl are at times referred to herein as
the derivatized embodiments of the compounds of the
present invention.
20 It can also be seen in the definition of
formula (1) that R^2 can be a substituent of the
formula $-L-X-(L-R-(OCH=CH-CH_2R^1)_n)_1$. In these
embodiments, a central moiety X is substituted with a
total of (i+1) substituents of the formula
25 $(-L-R-(OCH=CH-CH_2R^1)_n)$. Suitable X groups include, but
are not limited to -Ph- groups, wherein -Ph- is
phenylene (i.e. 1,2-phenylene, 1,3-phenylene, or 1,4-
phenylene), as well as -Ph-Ph-;

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1 $\text{-Ph}_{0.1}\text{-C}_a\text{H}_{2s}\text{-Ph}_{0.1}$ groups in which C_aH_{2a} is an alkylene
group containing 1 to 20 carbon atoms; and groups
consisting of a C_fH_{2f} and a C_gH_{2g} moiety which are
bonded to -C(O)- , -O- , -C(O)O- , -Ph- or -C(O)NH- and f
and g are each 1 to 12. The C_aH_{2a} , C_fH_{2f} and C_gH_{2g} groups
5 can be straight or branched, and they can be attached
to adjacent moieties at the same carbon atom (e.g.
 $\text{-CH}_2\text{-}$, CH_3CCH_3) or at different carbon atoms (e.g.
 $\text{-CH}_2\text{CH}_2\text{-}$, $\text{-CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$).

10 In formula (1), L represents a linking group
between the X moiety in each of the substituted R
groups. Suitable linking groups L include a single
chemical bond, -C(O)O- , -OC(O)O- , -O- , and -NHC(O)O-
bearing in mind that in any case each R group is
bonded to an oxygen atom of the linking group L.
15 Also, when L is a chemical bond, X can be -C(O)- .

Specific preferred examples of compounds in
accordance with this description are provided
hereinbelow.

20 The choice of routes for synthesizing the
compounds of the present invention is dictated
principally by the particular target compound desired.
As will be seen below, in many cases there are several
different routes available to synthesize a particular
compound.

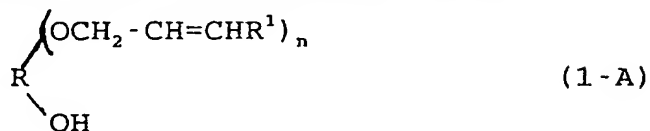
25 To synthesize those embodiments of the
present invention wherein R^2 is -OH , the preferred
route is isomerization of the allyl ether analog of

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the desired propenyl compound. Those allyl ether
1 analogs thus have the formula (1-A)



5 wherein R, R₁ and n are as defined herein. This allyl precursor, if not available commercially, can be prepared by reacting a precursor of formula R(OH)_{n+1} with an appropriate number of moles of an allyl
10 chloride of the formula Cl-CH₂-CH=CHR¹ (or the corresponding bromide) calculated to provide the desired hydroxyl substituted compound of formula (1-A).

The allyl ether precursor of formula (1-A)
15 is converted to the desired propenyl product by isomerization of the allyl compound. This isomerization is carried out in the presence of a small but effective amount of a catalyst for the isomerization, in the presence or absence of a solvent
20 which is inert to the reactant, product and catalyst. Catalysts for the isomerization include strong bases, such as potassium t-butoxide-DMSO, and sodium amide. Other suitable catalysts for this isomerization include transition metal-containing catalysts, such as
25 tris(triphenylphosphine) ruthenium (II) dichloride, tris(triphenylphosphine) rhodium (I) chloride, ruthenium on alumina, and iron pentacarbonyl.

While complete isomerization of all allyl groups present to propenyl is preferred, it is also
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1 contemplated that some but not all allyl groups
isomerize to propenyl.

Compounds of formula (I) wherein R^2 is
alkoxy, phenoxy, acryloyloxy, methacryloyloxy, or A-
(Het)_{0.1}-C(O)O- can be synthesized in either of two
5 ways. One way involves the formation of the propenyl-
substituted compound as described above wherein R^2 is
hydroxyl, followed by derivatization of the hydroxyl-
substituent by reaction thereof with a suitable
reagent by which the desired R^2 group replaces the
10 hydroxyl group. For instance, when the desired R^2
group is alkoxy, the corresponding hydroxyl-
substituted compound can be reacted with the
corresponding alkyl halide, such as alkyl bromide,
under alkaline conditions. When the desired R^2 group
15 is phenoxy; the hydroxyl-substituted compound of
formula (1) can be reacted with p-toluene sulfonyl
chloride to form an intermediate tosylate ester, which
is then reacted with phenol to form the desired
phenoxy compound. Acyloxy derivatives such as
20 acryloyloxy, methacryloyloxy, A-O-C(O)O- and A-C(O)O-
derivatives can be formed by reacting the
corresponding acyl chloride or anhydride with the
compound of formula (1) wherein R^2 is -OH. The
urethane derivatives, of the formula A-NH-C(O)O- can
25 be formed by reacting the corresponding isocyanate
with a compound of formula wherein R^2 is -OH.

Another route for synthesizing compounds of
formula (1) involves first reacting the allyl ether
precursor having formula (1-A) to derivatize the
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hydroxyl group by employing any of the procedures
1 available for derivatizing the hydroxyl-substituted
propenyl compound, so as to form a suitably
derivatized allyl compound, and then isomerizing the
derivatized allyl compound to the desired propenyl
5 product. The isomerization conditions and catalysts
suitable for the isomerization are the same as
described hereinabove with respect to isomerization of
compounds of formula (1-A).

To produce compounds of the formula (1)
10 wherein the R^2 substituent contains a linking group L
as defined hereinabove, it is preferred first to react
the allyl analog wherein R^2 is hydroxyl, with a
compound corresponding to the formula $X-(L-Z)_{i+1}$. For
this reactant, X is as defined above and the linking
15 groups L are as defined hereinabove. The terminal
group Z is any capping group which will leave the L
group (or, when L is a chemical bond, leave the X
group) upon reaction with the hydroxyl-substituted
allyl reactant so as to permit formation of the
20 desired linkage between the L groups and R groups.
For instance, when the L groups are to be ester
linkages between the X group and the respective R
moieties, the group Z can be hydrogen or lower alkyl
such that the reaction between the precursor $X(-L-Z)_{i+1}$
25 is a matter of esterification or transesterification.
Other routes and suitable reactants permitting the
incorporation of other L linking groups disclosed
herein will be apparent to those of ordinary skill in
this art.

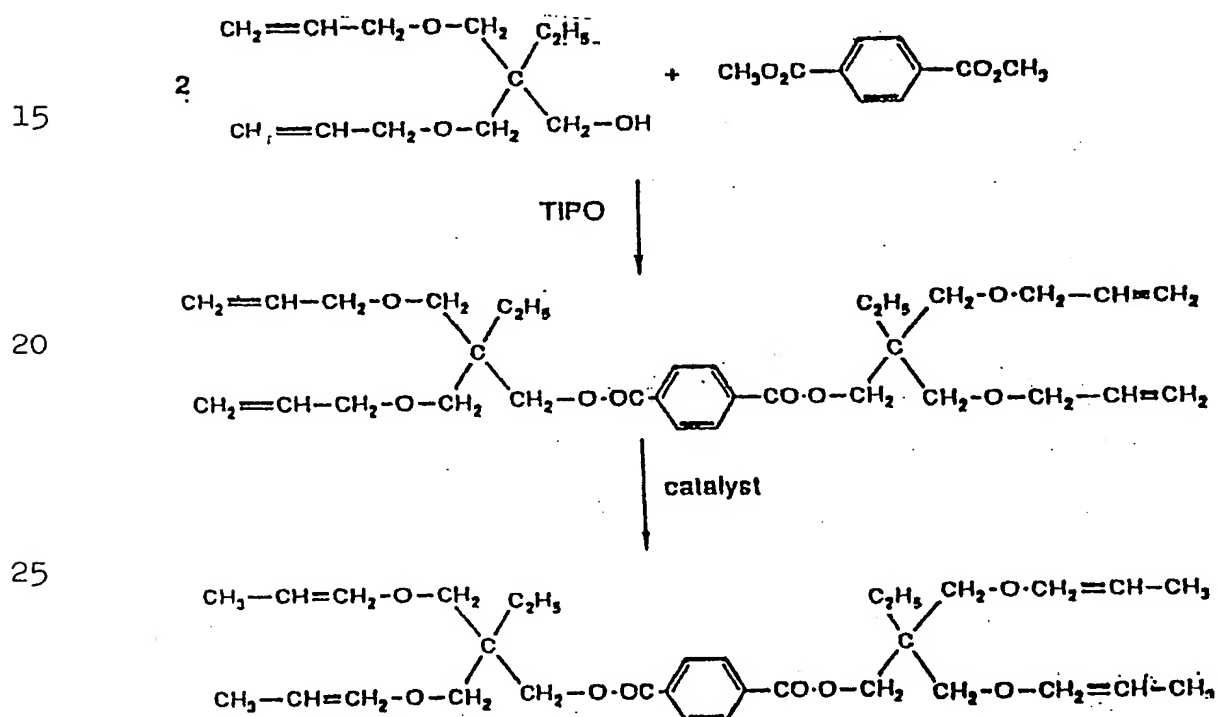
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Following formation of the intermediate allyl analog in this manner, the intermediate is isomerized in the presence of any of the isomerization catalysts described hereinabove to form the product propenyl derivative having a plurality of propenyloxy groups attached to the X moiety through the R moiety and the L linking groups.

One example of the synthesis of such a multifunctional compound is the following: (termed herein Scheme A):

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Analogous compound where the 1,4-phenylene
1 is replaced by linear, branched or cyclic alkylene, or
by other position isomers of phenylene, can be made by
the same procedure from the appropriate diester.

Compounds containing -C(O)- in place of the
5 - (O)CC₆H₄C(O)- moiety in Scheme A can be prepared by an
analogous procedure from the diallyl precursor and
diethyl carbonate in the presence of TIPO, (titanium
tetra-isopropoxide) to form the allyl analog of the
desired final product, followed by catalytic
10 isomerization of the allyl groups to propenyl.

Compounds containing phenylene or straight,
branched or cyclic alkylene in place of the -
(O)CC₆H₄C(O)- moiety on Scheme A can be prepared by
reacting the diallyl precursor and X-(hal)₂, wherein
15 hal is chlorine, bromine or iodine, in the presence of
e.g. NaOH or KOH, to form the allyl analog of the
desired final product, followed by catalytic
isomerization of the allyl groups to propenyl.

Compounds containing a - (O)CNH-X-NHC(O)
20 linkage in place of the - (O)CC₆H₄C(O)- moiety in Scheme
A can be prepared by reacting the diallyl precursor
with the polyisocyanate X(NCO)₄ in the presence of
e.g. stannous octoate to form the analog of the
desired final product, followed by catalytic
25 isomerization of the allyl groups to propenyl.

Compounds containing a - (O)CO-X-OC(O)-
linkage in place of the - (O)CC₆H₄C(O)- moiety in Scheme
A can be prepared by reacting the diallyl precursor
with X(OC(O)Cl)₄ in the presence of e.g. tributylamine
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1 to form the allyl analog of the desired final product,
followed by catalytic isomerization of the allyl
groups to propenyl.

5 The propenyl compounds of formula (1) are
readily polymerized by exposure to ultraviolet or
electron beam radiation in the presence of a cationic
photoinitiator. Among those photoinitiators which may
be used to achieve polymerization are diazonium salts,
diaryliodonium salts, triarylsulfonium salts,
diaryliodosonium salts, triarylsulfoxonium salts,
10 dialkylphenacylsulfonium salts, and dialkyl-4-
hydroxyphenylsulfonium salts. Typically, these salts
contain complex metal halide or other non-nucleophilic
ions such as BF_4^- , PF_6^- , SbF_6^- , AsF_6^- , ClO_4^- , CF_3SO_3^- ,
(C_6F_5) $_4\text{B}^+$ and the like. Examples of suitable
15 photoinitiator salts are described hereinbelow and
include those described in Crivello and Dietliker, in
Chemistry & Technology of UV & EB Formulation For
Coatings, Inks & Paints, Vol. 3, 1991, page 329, the
disclosure of which is hereby incorporated herein by
20 reference.

The amount of photoinitiator should be in
the range of about 0.1 to 10% by weight based on the
weight of the compound or compounds of formula (1).
As noted herein, the compositions containing compounds
25 of formula (1) and one or more photoinitiators for
polymerization of such compounds comprises one aspect
of the present invention.

Rapid and complete polymerization of the
compounds of formula (1) can be achieved by
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irradiating the composition with an electron beam dose
1 on the order of 0.1 to 10 Mrad or ultraviolet
radiation flux on the order of 10-30 mW/cm². Higher
energy levels are also useful, especially when higher
throughput speeds are desired or thicker masses of
5 polymer are presented.

Photopolymerizable compositions containing
the compounds for formula (I) can also contain any of
the other additives customary for such uses, in the
amounts thereof adequate to enable the additive to
10 perform its desired function. Such additives include
photosensitizers, fillers, flow control agents and the
like. Examples of suitable materials for providing
these functions abound in this field and are well
known to those experienced in this field, and include
15 the materials which are employed for those functions
with other radiation-curable monomers such as
acrylates and vinyl ethers. In addition, other
comonomers may be present such as epoxies, vinyl
ethers and 1-butenyl ethers.

20 Films and coatings formed by irradiation of
compositions containing any of the compounds of
formula (I) exhibit satisfactory and even superior
mechanical strength, adhesion to substrate, high
temperature stability, and high reactivity. It is not
25 necessary to formulate the photo-polymerizable or
electron beam-polymerizable composition in a solvent,
thus permitting the operator to avoid the hazards and
inconvenience of using solvents.

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The following Table 1 identifies particular
1 R² substituents which are referred to in the following
examples and discussion:

5

Table 1

10	Substituent No.	Substituent
	1	OCH ₃
	2	OC ₄ H ₉
	3	OC ₈ H ₁₇
	4	OC ₆ H ₅
15	5	OC (O) CH ₃
	6	OC (O) CH=CH ₂
	7	OC (O) OC ₄ H ₉
	8	OC (O) NHC ₄ H ₉
20	9	OC (O) NHC ₆ H ₅

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1 In the following Examples, derivatives of
trimethylolpropane diallyl ether and of
trimethylolpropane dipropenyl ether were prepared.
The diallyl ether derivatives are identified with the
number of the substituents in the R² position followed
5 by the letter A, and dipropenyl ether derivatives are
identified with the number of the substituent in the
R² position followed by the letter P.

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Examples

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¹H-NMR spectra were recorded either on a Varian XL-200 MHz or Unity 500 MHz spectrometer at room temperature in CDCl₃. Elemental analyses were performed by Atlantic Microlabs Inc, Norcross, GA. Routine infrared spectra were obtained on a Midac FT-IR. Real-time IR were recorded on a Midac FT-IR (Midac Corp., Irvine, CA) equipped with a liquid nitrogen cooled MCT-detector at a scan rate of 270 scans per minute and a resolution of 4 cm⁻¹. The data was recorded using the software program LabCalc (Galactic Software, Salem CT) and processed with Grams/386 (Galactic Software, Salem CT). The FT-IR was equipped with a UVEXS Co. Model SCU 110 UV lamp fitted with a fiber optical cable. The UV radiation flux on the sample was 17-18 mW/cm².

Trimethylolpropane Di(1-propenyl) methyl ether (1P)

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Trimethylolpropane diallyl ether (20 g, 93 mmol), 14.1 g (112 mmol) of dimethyl sulfate, 4.48 g (112 mmol) of powdered sodium hydroxide and 50 mL of toluene were combined in a three neck round bottom flask equipped with a thermometer, overhead stirrer and a reflux condenser. The suspension was stirred for 10 minutes at 40°C. Tetra-n-butylammonium bromide (0.2 g) were added and the suspension was heated to 110°C for 6 hours. The solution was cooled to room temperature, extracted with a 1 M sodium hydroxide

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1 solution, washed three times with water and the
solvent was evaporated. The residue was subjected to
fractional distillation under reduced pressure (b.p.
55°C/0.3 mm, Yield: 19.4 g; 91%).

5 ¹H-NMR (CDCl₃): δ(ppm) 0.84 (t, 3H), 1.42 (quart., 2H),
3.28 (s, 2H), 3.34 (s, 7H), 3.96 (d, 4H), 5.16 (d, 2H),
5.25 (d, 2H), 5.89 (m, 2H)

10 Allyl ether 1A (17 g, 74 mmol) and 0.02 g (22
μmol) of tris(triphenylphosphine)ruthenium (II)
dichloride were heated under nitrogen for 1 hour to
160°C. The propenyl ether 1P was distilled under
reduced pressure (b.p. 48°C/0.25mm; Yield: 16.7 g,
98%).

15 ¹H-NMR (CDCl₃): δ=0.84 (m, 3H), 1.42 (m, 2H), 1.56
(d, 3H, CH₃ trans-propenyl ether), 1.59 (d, 3H, CH₃ cis-
propenyl ether), 3.28 (s, 2H), 3.35 (s, 3H), 3.52 (s, 2H,
trans-propenyl ether), 3.62 (s, 2H, cis-propenyl ether),
20 4.33 (m, 1H, cis-propenyl ether), 4.78 (m, 1H, cis-
propenyl ether), 5.95 (m, 1H, cis-propenyl ether), 6.21
(d, 1H, trans-propenyl ether)

25 Elemental Analysis: Calculated for C₁₃H₂₄O₃, C,
68.38 %, H, 10.59%.
Found C: 68.36%; H, 10.55%

Synthesis of Trimethylolpropane Di(1-propenyl) Butyl
(2A) and Octyl (3A) Ethers

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Trimethylolpropane diallyl ether (10 g, 46.7 mmol), 93.3 mmol of n-butyl or n-octyl bromide, 15.7g of potassium hydroxide and 90 mL of DMSO were stirred for two hours at room temperature. The solution was diluted with 200 mL of water and extracted twice with 50 mL of ethyl acetate. The combined organic phases were washed with water and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure yielding 67% 2A (b.p. 110°C/0.1mm).

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$^1\text{H-NMR}$ (CDCl_3): δ (ppm)=0.84 (m,6H), 1.35 (quint.,2H), 1.42 (quart.,2H), 1.57 (quint.,2H), 3.28 (s,2H), 3.34 (s,4H), 3.40 (t,2H), 3.96 (d,4H), 5.16 (d,2H), 5.25 (d,2H), 5.89 (m,2H)

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In a similar fashion, 3A (b.p.145°C/0.05 mm) was prepared in 56% yield.

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$^1\text{H-NMR}$ (CDCl_3): δ (ppm)=0.84 (m,6H), 1.25-1.36 (m,8H), 1.42 (quart., 2H), 1.53 (quint.,2H), 3.28 (s,2H), 3.32 (s,4H), 3.39 (t,2H), 3.96 (d,4H), 5.16 (d,2H), 5.25 (d,2H), 5.89 (m,2H)

25

Both of the allyl ethers 2A and 3A were isomerized completely by heating at 170°C for 1 hour with 0.02 g (22 μmol) of tris(triphenylphosphine)ruthenium(II)dichloride as the catalyst.

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Trimethylolpropane di(1-propenyl) n-butyl
1 ether 2P (b.p. 113°C/0.2mm) was obtained in a 95%
yield.

¹H-NMR (CDCl₃): δ(ppm)=0.82-0.90 (m,6H), 1.38 (m,2H)
5 1.38-1.59 (m,12H), 3.28 (s,2H), 3.39 (t,2H), 3.55
(s,2H,trans-propenyl ether), 3.64 (s,2H,cis-propenyl
ether), 4.33 (m,1H,cis-propenyl ether), 4.78 (m,1H
trans-propenyl ether), 5.95 (m,1H,cis-propenyl ether),
10 6.12 (d,1H,trans-propenyl ether)

Elemental Analysis: Calculated for C₁₆H₃₀O₃:C, 73.57%;
H:11.73%.

Found: C, 73.63%; H, 11.70%.

15 Trimethylolpropane di(1-propenyl)n-octyl
ether 3P was obtained in 98% yield (b.p. 155°C/0.1
mm).

¹H-NMR (CDCl₃): δ(ppm)=0.80-0.91 (m,6H), 1.22-1.61
20 (m,22H) 3.30 (s,2H), 3.39 (m,2H), 3.55 (s, 2H, trans-
propenyl ether), 3.64 (s,2H, cis-propenyl ether), 4.33
(m,1H, cis-propenyl ether), 4.78 (m,1H, trans-propenyl
ether), 5.95 (m,1H, cis-propenyl ether), 6.12 (d,1H,
trans-propenyl ether)

25 Elemental Analysis: Calculated for C₂₀H₃₈O₃:C, 73.57%;
H, 11.73%

Found: C, 73.63%; H, 11.70%.

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-19-

1 Synthesis of Trimethylolpropane Di(1-propenyl) phenyl
Ether (4A)

5 Trimethylolpropane diallyl ether (30 g, 140
mmol), 50 mL of pyridine and 50 mL of toluene were
combined in a two neck flask. The solution was heated
to 60°C and 38.13 g (200 mmol) p-toluenesulfonyl
chloride dissolved in 100 mL of chloroform were added
dropwise over a period of 1 hour. The solution was
stirred at 60°C for an additional three hours. After
cooling to room temperature, the solution was
10 extracted with saturated sodium bicarbonate solution
until no more carbon dioxide was evolved. After
washing three times with water, the solvent was
evaporated and the crude product used for further
reactions. The yield of trimethylolpropane diallyl
15 ether tosylate ester was 46.1 g (89%).

20 ¹H-NMR (CDCl₃): δ(ppm) 0.79 ppm (t, 3H), 1.39 (quart., 2H),
2.42 (s, 3H), 3.22 (s, 4H), 3.83 (d, 4H), 3.96 (s, 2H),
5.14 (d, 2H), 5.19 (d, 2H), 5.89 (m, 2H), 7.32 (d, 2H),
7.78 (d, 2H)

25 Elemental Analysis: Calculated for C₁₉H₂₈O₅: C, 61.93%; H,
7.66%.

Found: C, 61.77%; H, 7.61%

30 Potassium tert-butoxide (3.04 g, 27.1 mmol)
were dissolved in 30 mL of DMSO. Phenol (2.55 g, 27.1
mmol) was added and the solution heated under nitrogen
to 70°C. There were added 5 g (13.57 mmol) of

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1 trimethylolpropane diallyl ether tosylate and the dark
solution was stirred at 70°C for 6 hours. After
cooling, the solution was diluted with 70 mL water and
then extracted twice with 60 mL ethyl acetate. The
5 combined organic extracts were washed three times with
50 mL portions of water, dried over Na₂SO₄ and the
solvent removed by evaporation. The residue was
distilled under reduced pressure (0.1 mm) at 150°C to
give 2.01 g (51%) of colorless liquid 4A.

10 ¹H-NMR (CDCl₃): δ = 0.90 ppm (t, 3H), 1.57 (quart., 2H) 3.42
(s, 4H), 3.88 (s, 2H), 3.96 (d, 4H), 5.16 (d, 2H), 5.25
(d, 2H), 5.89 (m, 2H), 6.91 (m, 3H), 7.24 (m, 2H)

The allyl ether was quantitatively
15 isomerized at 175°C for 1 hour with 0.02 g (22 μmol)
of tris(triphenylphosphine)ruthenium (II) dichloride
as the catalyst. The yield of 4P (b.p. 155°C/0.2 mm)
was 97%.

20 ¹H-NMR (CDCl₃): δ (ppm) 0.90 (m, 3H), 1.50-1.64 (m, 8H),
3.65 (d, 2H, trans-propenyl ether), 3.78 (d, 2H, cis-
propenyl ether), 3.88 (t, 2H), 4.37 (m, 1H, cis-propenyl
ether), 4.78 (m, 1H, trans-propenyl ether), 5.95 (m, 1H,
cis-propenyl ether), 6.22 (d, 1H, trans-propenyl ether),
25 6.91 (m, 3H), 7.24 (m, 2H)

Elemental Analysis: Calculated for C₁₈H₂₆O₃:
C, 74.45%; H, 9.02 %.

Found: C, 74.55%; H, 9.02%

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- 21 -

1 Synthesis of Trimethylolpropane Di(1-propenyl)ether
Acetate(5P)

5 Trimethylolpropane diallyl ether (20 g, 93.3
mmol) and 12.4 mL (121 mmol) of acetic anhydride were
dissolved in 40 mL of toluene. One drop of pyridine
was added and the solution heated to reflux for 16 h.
After cooling, the solution was extracted with
10 saturated sodium bicarbonate solution until no more
gas was evolved. The solution was washed with water,
and the organic layer separated and dried over
anhydrous sodium sulfate. The solvent was removed on
a rotary evaporator and the residue distilled under
reduced pressure. The fraction boiling at 76°C/0.025
15 mm was collected. The yield of 5A was 22.7 g (95%).

¹H-NMR (CDCl₃):δ(ppm) 0.83 (t,3H), 1.43 (quart.,2H),
2.05 (s,3H), 3.33 (s,4H), 3.93 (d,4H), 4.03 (s,2H),
5.15 (d,2H), 5.24 (d,2H), 5.87 (m,2H)

20 The isomerization of 5A to 5P was conducted
with tris(triphenylphosphine)ruthenium (II) dichloride
as the catalyst at 190°C under N₂. After 20 minutes
the conversion to the propenyl ether 5P was complete
as determined by ¹H-NMR. The product was purified by
25 fractional vacuum distillation to yield compound 5P in
97% overall yield (b.p. 82°C/0.05 mm).

¹H-NMR (CDCl₃):δ(ppm) 0.87 (m,3H), 1.46 (m,2H), 1.53-
1.59 (m,6H), 2.06 (s,3H), 3.57 (d,2H,trans-propenyl

-22-

ether), 3.63 (d, 2H, cis-propenyl ether), 4.02 (t, 2H),
1 4.37 (m, 1H, cis-propenyl ether), 4.77 (m, 1H, trans-
propenyl ether), 5.91 (m, 1H, cis-propenyl ether), 6.21
(d, 1H, trans-propenyl ether)

5 Elemental Analysis: Calculated for $C_{14}H_{24}O_4$: C, 65.60%;
H, 9.44%
Found: C, 65.49%; H, 9.48%

10 Preparation of Trimethylolpropane Di(1-propenyl) Ether
Acrylate (6P)

There were combined 10 g (47 mmol) of
trimethylolpropane diallyl ether, 30 g (0.234 mol) of
n-butyl acrylate and 0.5 g of titanium (IV) tetra
15 isopropoxide (TIPO) was added. The solution was
stirred under nitrogen at 150°C for 10 hours. After
this time, the solvent and the excess n-butyl acrylate
were removed by distillation under reduced pressure.
The fraction boiling at 112°C/0.05 mm was collected.
20 The yield of 6A was 7.06 g (56%).

1H -NMR ($CDCl_3$): δ (ppm) 0.87 (t, 3H), 1.43 (quart., 2H),
3.36 (s, 4H), 3.92 (d, 4H), 4.12 (s, 2H), 5.15 (d, 2H),
5.22 (d, 2H), 5.79-5.89 (m, 3H), 6.12 (m, 1H), 6.39
25 (d, 1H)

Elemental Analysis: Calculated for $C_{15}H_{24}O_4$: C, 67.14%;
H, 9.01%.
Found: C, 67.21%; H, 9.12%.

30

35

- Allyl ether 6A was quantitatively isomerized as described in the previous examples by heating for 20 minutes at 190°C under nitrogen. The conversion was complete after 25 minutes. The distilled product was extremely sensitive to air and polymerization took place upon exposure to air. Attempts to stabilize the compound by adding such free radical inhibitors as hydroquinone and tert.-butyl catechol also resulted in polymerization during the isomerization reaction.
- ¹H-NMR (CDCl₃): δ(ppm) 0.87 (m, 3H), 1.50 (m, 8H), 3.58 (d, 2H), 3.65 (d, 2H), 4.15 (t, 2H), 4.38 (m, 1H, cis-propenyl ether), 4.77 (m, 1H, trans-propenyl ether), 5.80-6.41 (m, 5H)
- Preparation of 1-Propenyl Ether Substituted Urethanes 8P and 9P

Combined in a 100 mL round bottom flask equipped with a magnetic stirrer, reflux condenser and nitrogen inlet were 10 g (46.7 mmol) of trimethylolpropane diallyl ether and 61 mmol of either phenyl isocyanate or n-butyl isocyanate, then 0.01 g (0.15 mmol) of di-n-butyltin dilaurate were added. The solutions were stirred at room temperature for 30 minutes and then heated to 60°C and stirred for an additional 30 minutes. After cooling, the products were purified by distillation in a Büchi microdistillation apparatus.

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8A was obtained in 97% yield with a b.p. of
1 180°C/0.1 mm.

¹H-NMR (CDCl₃): δ(ppm) 0.85 (t, 3H), 0.92 (t, 3H), 1.32-
1.50 (m, 6H), 3.17 (m, 2H), 3.30 (s, 4H), 3.91 (d, 4H),
5 4.02 (s, 2H), 5.13 (d, 2H), 4.61 (s, 1H, NH), 5.24
(d, 2H), 5.86 (m, 2H).

9A was not distillable, and was purified by
removing the starting isocyanate by heating in the
10 microdistillation apparatus to 180°C for 1 h under
high vacuum (0.05 mm). The yield was 94%.

¹H-NMR (CDCl₃): δ(ppm) 0.87 (t, 3H), 1.46 (quart., 2H),
3.37 (s, 4H), 3.96 (d, 4H), 4.18 (s, 2H), 5.16 (d, 2H),
15 5.25 (d, 2H), 5.88 (m, 2H), 6.60 (s, 1H, NH), 7.05 (t,
1H), 7.30-7.41 (m, 4H).

Isomerizations of 8A and 9A were conducted with the
ruthenium catalyst under nitrogen.

20

8A was isomerized to 8P in 8% yield after 2h
at 180°C and purified by vacuum microdistillation
(b.p. 182°C/0.1 mm).

25 ¹H-NMR (CDCl₃): δ=0.80 - 0.95 ppm (m, 6H), 1.30-1.60
(m, 12H), 3.18 (m, 2H), 3.47 (d, 2H, trans-propenyl
ether), 3.62 (d, 2H, cis-propenyl ether), 4.04 (d, 2H),
4.38 (m, 1H, cis-propenyl ether), 4.62 (s, 1H, NH), 4.78

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(m, 1H, trans-propenyl ether), 5.93 (m, 1H, cis-propenyl
1 ether), 6.21 (d, 1H, trans-propenyl ether)

Elemental Analysis: Calculated for $C_{17}H_{31}NO_4$: C, 65.14%;
H, 9.97%; N, 4.47%.

5 Found: C, 65.89%; H, 10.18%; N, 4.05%.

9A was isomerized to 9P in 89% yield after
2h at 180°C. Purification was accomplished by vacuum
microdistillation (b.p. 190°C/0.025 mm).

10

1H -NMR ($CDCl_3$): δ =0.80 - 1 ppm (m, 6H), 1.45-1.70 (m, 8H),
3.69-3.80 (m, 4H), 4.20 (d, 2H), 4.39 (m, 1H, cis-
propenyl ether), 4.79 (m, 1H, trans-propenyl ether),
5.92 (m, 1H, cis-propenyl ether), 6.22 (d, 1H, trans-
15 propenyl ether), 6.81 (s, 1H, NH), 7.05 (t, 1H), 7.29-
7.40 (m, 4H)

Elemental Analysis: Calculated for $C_{19}H_{27}NO_4$: C, 68.44%;
H, 8.16%; N, 4.20%.

20 Found: C, 68.38%; H, 8.13%; N, 4.08%

UV Cure of Novel Monomers

Thin films (~25 μ m) of the liquid monomers
25 containing 0.5 mol% of IOC10 ((4-n-decyloxyphenyl)
phenyliodonium hexafluoroantimonate) photoinitiator
were drawn onto glass or steel panels and irradiated
using a GE H3T-7 200 W medium pressure mercury arc
lamp mounted at a distance of 12 cm from the sample.

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1 This apparatus was equipped with a mechanical shutter
which could be opened to expose the samples to UV
irradiation. With monomers 1P-7P, polymerization of
the monomers took place within 0.5-1 second to give
crosslinked solid films of the polymer. Monomer 8P
5 did not polymerize under these conditions while longer
irradiation times (1-2 minutes) were required to
polymerize monomer 9P.

The polymerizations were also followed in
detail by real-time infrared spectroscopy (RTIR), a
10 method described by Decker and Moussa in J. Polym.
Sci. Part a: Polym. chem., 28, 4329 (1990). For this
solutions of the photoinitiator (IOC10) in a
concentration of 0.5 mol% in the monomers were
prepared. The solution was coated on a commercially
15 available Saran® film (polyvinylidene chloride). The
films were then covered by a second Saran film and
this assembly mounted in conventional 5 x 5 cm slide
frames. This sandwich was placed in a horizontally
mounted Midac Corp. FT-IR spectrometer. The
20 instrument was equipped with a UVEXS Co. Model SCU 110
UV lamp fitted with a fiber optic cable and the probe
of the fiber optic cable positioned so as to direct UV
irradiation onto the sample window of the
spectrometer. UV intensity was measured with the aid
25 of a Control Cure Radiometer and found to be 18-19
mW/cm². To determine the rate of polymerization the
IR band at 1660 to 1670 cm⁻¹ was followed. The
conversion was calculated by integrating the areas of
the peak at t_0 and t_{end} . The initial slopes of the
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curves ($R_p/[M]_0$) were determined and are considered to
1 be a measure of the reactivity of the monomers. In
these studies, the acrylate substituted monomer 6P was
not included since it is too unstable to be measured
under air without polymerizing by oxygen induction.
5 The results of the measurements are displayed and
summarized in Table 2.

The results show that the methyl ether
substituted monomer 1P has the highest rate of
polymerization. This is expected since it this
10 monomer does not contain polar groups which could
interfere with the propagating carbenium ions. In
addition, the methyl ether group is relatively small,
so that steric factors are also small. The n-butyl
and n-octyl ethers (2P and 3P) undergo rather sluggish
15 photopolymerizations with IOC10. The reason for the
surprisingly low rates of polymerization is the
limited solubility of the photoinitiator (IOC10) in
these monomers. In contrast, when the polymerization
is carried out using the much more soluble
20 commercially available di(dodecylphenyl)iodonium
hexafluoroantimonate (UV 9380C), both monomers
polymerize very rapidly and to high conversions. The
n-octyl ether, 3P, polymerizes with a higher
conversion of the propenyl ether groups than the n-
25 butyl ether 2P. One reason may be when the former
monomer is polymerized a polymer which possesses a
lower glass transition temperature is produced.

30

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Monomer	Photoinitiator*	PI conc. (mol%)	Slope ($R_p [M_0] (s^{-1})$)	Conversion (300s) (%)
1P	IOC10	0.5	5.3	74
2P	IOC10	0.5	0.25	40
2P	UV9380C	0.5	2.0	67
3P	IOC10	0.5	0.7	64
3P	UV9380C	0.5	2.9	75
4P	IOC10	0.5	1.8	65
5P	IOC10	0.5	2.7	74
7P	IOC10	0.5	2.6	75
8P	IOC10	0.5	0	0
8P	IOC10	2.0	0	0
9P	IOC10	0.5	0.06	10
9P	IOC10	1.0	0.4	27
9P	IOC10	2.0	0.5	30

* -IOC10 is (4-n-decyloxyphenyl)iodonium hexafluoroantimonate and UV 9380C is di(dodecylphenyl)phenyliodonium hexafluoroantimonate

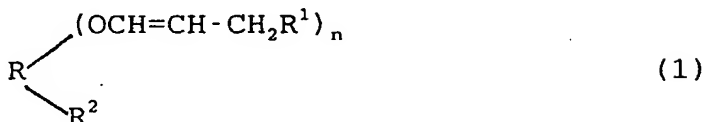
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What Is Claimed Is:

1

1. A compound of the formula (1)

5



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl
 10 containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

R² is -OH, alkoxy containing 1 to 20 carbon
 atoms which is optionally substituted with phenyl and
 two consecutive carbon atoms of which are optionally
 15 bonded to an oxygen atom to form an epoxy ring,
 phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)_{0.1}-
 C(O)O- wherein A is alkyl containing 1 to 20 carbon
 atoms, and (Het) is -O- or -NH-;

or R² is -L-X-(L-R-(OCH=CH-CH₂R¹)_n)_i wherein
 20 up to (n-1)-OCH=CH-CH₂R₁ groups can instead be
 -OCH₂CH=CHR¹;

wherein X has any of the structures -Ph_{0.1}-C_aH_{2a}-Ph_{0.1}-Ph_{0.1}-(cyclo-C₅₋₂₀-alkyl)-Ph_{0.1}-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

25 -C_fH_{2f}C(O)C_gH_{2g} -C_fH_{2f}OC_gH_{2g}-, -C_fH_{2f}C(O)OC_gH_{2g}-, -C_fH_{2f}PhC_gH_{2g}-,
 or -C_fH_{2f}C(O)NHC_gH_{2g}-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

provided that each R is bonded to an oxygen atom of L,

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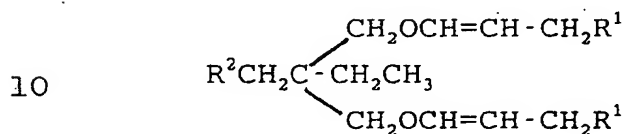
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and i is an integer from 1 to 3; or X is -C(O)-, each
 1 L is a chemical bond, and i is 1.

2. A compound according to claim 1 wherein
 R¹ is -H.

5

3. A compound according to claim 1 of the
 formula



4. A compound according to claim 1 of the
 15 formula
 $\text{R}^2-\text{CH}_2\text{C}(\text{CH}_2\text{OCH}=\text{CH}-\text{CH}_2\text{R}^1)_3$

5. A compound according to claim 1 wherein
 R² is -OCH₃, -OC₄H₉, -OC₈H₁₇, -OC₆H₅, -OC(O)CH₃,
 20 -OC(O)CH=CH₂, -OC(O)OC₄H₉, -OC(O)NHC₄H₉ or -OC(O)NH-C₆H₅.

6. A compound according to claim 1 wherein
 R¹ is -H and R² is -OC(O)-C₆H₄-C(O)O-R-(OCH=CHCH₃)₂.

25 7. A composition comprising a compound
 according to claim 1 and an effective amount of a
 photoinitiator for radiation-induced polymerization
 thereof.

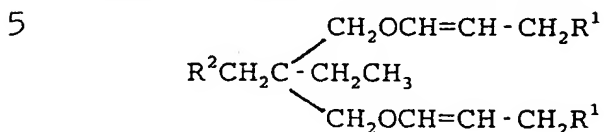
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8. A composition according to claim 7
 1 wherein R^1 is -H.

9. A composition according to claim 7
 wherein said compound has the formula



10. A composition according to claim 7
 10 wherein said compound has the formula



11. A composition according to claim 7
 15 wherein R^2 is $-OCH_3$, $-OC_4H_9$, $-OC_8H_{17}$, $-OC_6H_5$, $-OC(O)CH_3$,
 $-OC(O)CH=CH_2$, $-OC(O)OC_4H_9$, $-OC(O)NHC_4H_9$ or $-OC(O)NH-C_6H_5$.

12. A composition according to claim 7
 wherein R^1 is -H and R^2 is $-OC(O)-C_6H_4-C(O)O-R-$
 20 $(OCH=CHCH_3)_2$.

13. A process for forming a polymer
 comprising (a) forming a mixture comprising one or
 more compounds according to claim 1 and at least one
 25 cationic photoinitiator for polymerization of said
 compound, and

(b) irradiating said mixture with
 ultraviolet light or electron beam radiation of an

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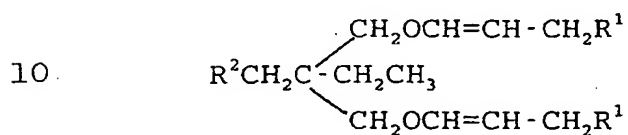
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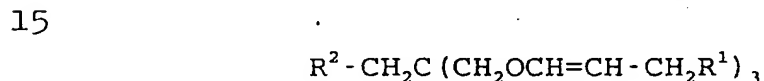
energy level, and for a time, sufficient to polymerize
 1 said one or more compounds.

14. A process according to claim 13 wherein
 5 R^1 is -H.

15. A process according to claim 13 wherein
 said compound has the formula



16. A process according to claim 13 wherein
 said compound has the formula



17. A process according to claim 13 wherein
 R^2 is $-OCH_3$, $-OC_4H_9$, $-OC_8H_{17}$, $-OC_6H_5$, $-OC(O)CH_3$,
 20 $-OC(O)CH=CH_2$, $-OC(O)OC_4H_9$, $-OC(O)NHC_4H_9$ or $-OC(O)NH-C_6H_5$.

18. A process according to claim 13 wherein
 R^1 is -H and R^2 is $-OC(O)-C_6H_4-C(O)O-R-(OCH=CHCH_3)_2$.

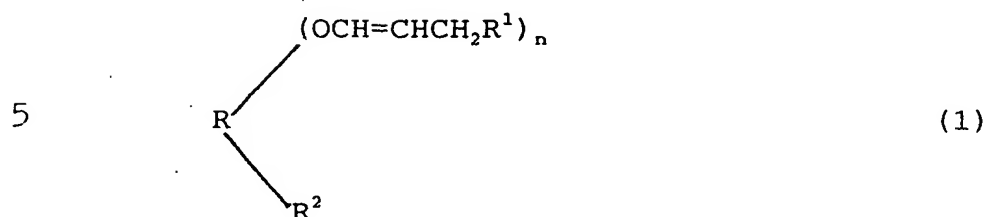
19. A product produced by the process of
 25 any one of claims 13 to 18.

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20. A process of making a compound of the
 1 formula (1)



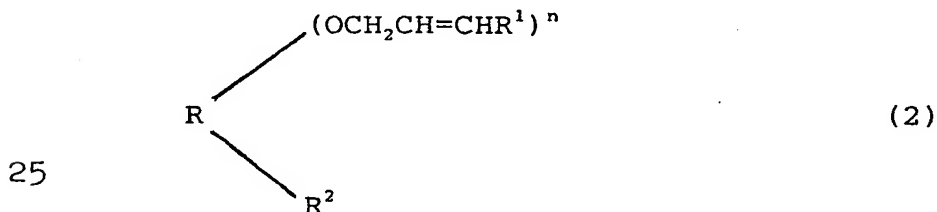
wherein n is an integer from 1 to 3;

10 R is linear, branched or cyclic alkyl
 containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

R² is -OH, alkoxy containing 1 to 20 carbon
 atoms which is optionally substituted with phenyl and
 15 two consecutive carbon atoms of which are optionally
 bonded to an oxygen atom to form an epoxy ring,
 phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)₀₋₁-
 C(O)O- wherein A is alkyl containing 1 to 20 carbon
 atoms, and (Het) is -O- or -NH-;

20 comprising isomerizing a compound of the formula (2)



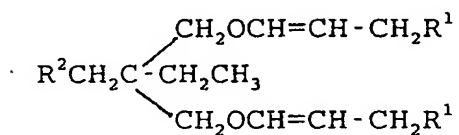
to said compound of the formula (1) in the presence of
 an effective amount of a catalyst for said
 isomerization.

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21. A process according to claim 20 wherein
 1 R^1 is -H.

22. A process according to claim 20 wherein
 5 said compound has the formula

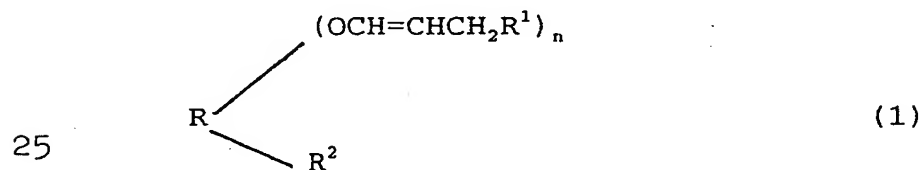


23. A process according to claim 20 wherein
 10 said compound has the formula



24. A process according to claim 20 wherein
 15 R^2 is $-\text{OCH}_3$, $-\text{OC}_4\text{H}_9$, $-\text{OC}_8\text{H}_{17}$, $-\text{OC}_6\text{H}_5$, $-\text{OC}(\text{O})\text{CH}_3$,
 $-\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $-\text{OC}(\text{O})\text{OC}_4\text{H}_9$, $-\text{OC}(\text{O})\text{NHC}_4\text{H}_9$ or $-\text{OC}(\text{O})\text{NH}-\text{C}_6\text{H}_5$.

25. A process of making a compound of the
 20 formula (1)



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl
 containing 1 to 6 carbon atoms;

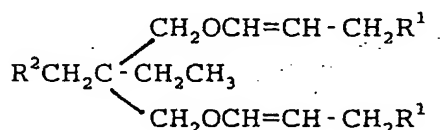
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R^1 is -H or $-CH_3$;

1 R^2 is alkoxy containing 1 to 20 carbon atoms
 which is optionally substituted with phenyl and two
 consecutive carbon atoms of which are optionally
 bonded to an oxygen atom to form an epoxy ring,
 5 phenoxy, acryloyloxy, methacryloyloxy, or $A-(Het)_{0.1}-$
 $C(O)O-$ wherein A is alkyl containing 1 to 20 carbon
 atoms, and (Het) is -O- or -NH-;
 comprising isomerizing an allyl compound of the
 formula $HO-R-(OCH_2CH=CHR^1)_n$ to a propenyl compound of
 10 the formula $HO-R-(OCH=CHCH_2R^1)$ in the presence of an
 effective amount of a catalyst for said isomerization,
 and then replacing the -OH group on said propenyl
 compound with R^2 .

15 26. A process according to claim 25 wherein
 R^1 is -H.

20 27. A process according to claim 25 wherein
 said compound has the formula



25 28. A process according to claim 25 wherein
 said compound has the formula



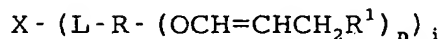
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- 36 -

29. A process according to claim 25 wherein
 1 R^2 is $-\text{OCH}_3$, $-\text{OC}_4\text{H}_9$, $-\text{OC}_8\text{H}_{17}$, $-\text{OC}_6\text{H}_5$, $-\text{OC}(\text{O})\text{CH}_3$,
 $-\text{OC}(\text{O})\text{CH}=\text{CH}_2$, $-\text{OC}(\text{O})\text{OC}_4\text{H}_9$, $-\text{OC}(\text{O})\text{NHC}_4\text{H}_9$ or $-\text{OC}(\text{O})\text{NH}-\text{C}_6\text{H}_5$.

30. A process of making a compound of the
 5 formula



wherein n is an integer from 1 to 3;

10 R is linear, branched or cyclic alkyl
 containing 1 to 6 carbon atoms;

R^1 is $-\text{H}$ or $-\text{CH}_3$;

wherein X has any of the structures $-\text{Ph}_{0.1}-\text{C}_a\text{H}_{2a}-\text{Ph}_{0.1}$
 $-\text{Ph}_{0.1}-(\text{cyclo}-\text{C}_{5.20}-\text{alkyl})-\text{Ph}_{0.1}-$, $-\text{Ph}-\text{Ph}-$, or $-\text{Ph}-$,

15 wherein Ph is phenylene and a is 1 to 20;

$-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{C}_g\text{H}_{2g}$, $-\text{C}_f\text{H}_{2f}\text{OC}_g\text{H}_{2g}$, $-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{OC}_g\text{H}_{2g}-$, $-\text{C}_f\text{H}_{2f}\text{PhC}_g\text{H}_{2g}-$,
 or $-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{NHC}_g\text{H}_{2g}-$, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

$-\text{C}(\text{O})\text{O}-$, $-\text{OC}(\text{O})\text{O}-$, $-\text{O}-$, or $-\text{NHC}(\text{O})\text{O}-$,

20 provided that each R is bonded to an oxygen atom of L ,
 and i is an integer from 1 to 3; or X is $-\text{C}(\text{O})-$, each
 L is a chemical bond, and i is 1.

comprising reacting an allyl compound of the
 formula $\text{HO}-\text{R}-(\text{OCH}_2\text{CH}=\text{CHR}^1)_n$ with a compound containing
 25 a moiety of the formula $\text{X}-(\text{L}-)_{i+1}$, to form an
 intermediate of the formula $\text{X}-(\text{L}-\text{R}-(\text{OCH}_2\text{CH}=\text{CHR}^1)_n)_{i+1}$
 and then isomerizing said intermediate to said
 compound of formula (1) in the presence of an
 effective amount of a catalyst for said isomerization.

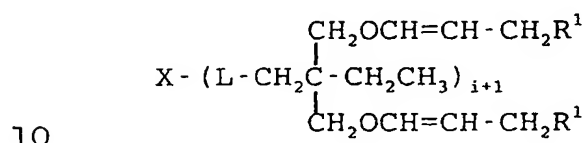
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- 37 -

1 31. A process according to claim 30 wherein
 R¹ is -H.

5 32. A process according to claim 30 wherein
 said compound has the formula



33. A process according to claim 30 of the
 formula



15 34. A process according to claim 30 wherein
 said compound has the formula
 $(\text{CH}_3\text{CH}=\text{CHO})_2-\text{R}-\text{OC}(\text{O})-\text{C}_6\text{H}_4-\text{C}(\text{O})\text{O}-\text{R}-(\text{OCH}=\text{CHCH}_3)_2$

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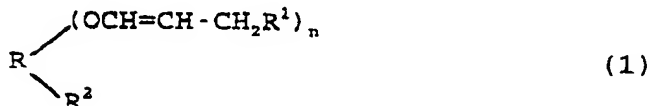
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AMENDED CLAIMS

[received by the International Bureau on 21 January 1999 (21.01.99);
original claims 1-34 replaced by new claims 1-21 (7 pages)]

1. A compound of the formula (1)



10 wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl
containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

15 R² is -OH, alkoxy containing 1 to 20 carbon
atoms which is optionally substituted with phenyl and
two consecutive carbon atoms of which are optionally
bonded to an oxygen atom to form an epoxy ring,
phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)_{0.1}-
C(O)O- wherein A is alkyl containing 1 to 20 carbon
20 atoms, and (Het) is -O- or -NH-;

or R² is -L-X-(L-R-(OCH=CH-CH₂R¹)_n)_i wherein
up to (n-1)-OCH=CH-CH₂R₁ groups can instead be
-OCH₂CH=CHR¹;

wherein X has any of the structures -Ph_{0.1}-C₆H_{2a}-Ph_{0.1}

25 -Ph_{0.1}-(cyclo-C₅₋₂₀-alkyl)-Ph_{0.1}-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

-C_fH_{2f}C(O)C_gH_{2g}-, -C_fH_{2f}OC_gH_{2g}-, -C_fH_{2f}C(O)OC_gH_{2g}-, -C_fH_{2f}PhC_gH_{2g}-,
or -C_fH_{2f}C(O)NHC_gH_{2g}-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

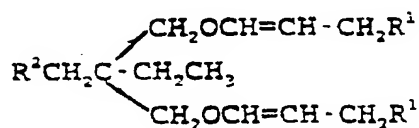
30 -C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

provided that each R is bonded to an oxygen atom of L, and i is an integer from 1 to 3; or X is -C(O)-, each L is a chemical bond, and i is 1.

5 2. A compound according to claim 1 wherein R¹ is -H.

3. A compound according to claim 1 of the formula

10



15 4. A compound according to claim 1 of the formula



20 5. A compound according to claim 1 wherein R² is -OCH₃, -OC₆H₅, -OC₈H₁₇, -OC₆H₅, -OC(O)CH₃, -OC(O)CH=CH₂, -OC(O)OC₆H₅, -OC(O)NHC₆H₅, or -OC(O)NH-C₆H₅.

6. A compound according to claim 1 wherein R¹ is -H and R² is -OC(O)-C₆H₄-C(O)O-R-(OCH=CHCH₃)₂.

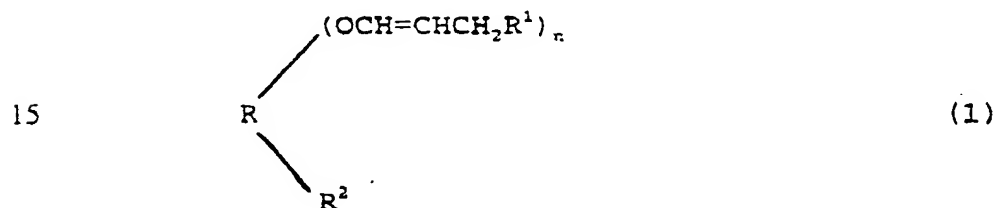
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7. A composition comprising a compound according to any one of claims 1-6 and an effective amount of a photoinitiator for radiation-induced polymerization thereof.

30

8. A process for forming a polymer comprising (a) forming a mixture comprising one or more compounds according to claim 1 and at least one cationic photoinitiator for polymerization of said compound, and
 5 (b) irradiating said mixture with ultraviolet light or electron beam radiation of an energy level, and for a time, sufficient to polymerize said one or more compounds.

10 9. A process of making a compound of the formula (1)



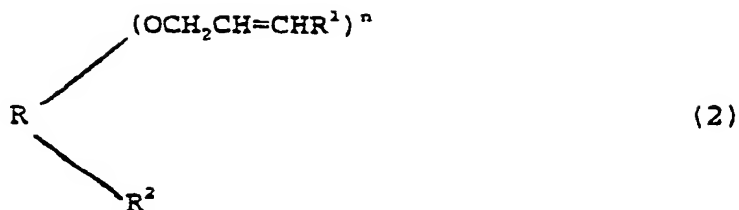
wherein n is an integer from 1 to 3;

20 R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

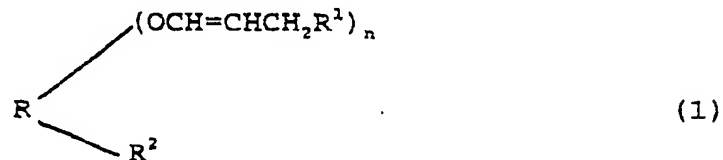
R² is -OH, alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and
 25 two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)_{0,1}-C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-;

30 comprising isomerizing a compound of the formula (2)



to said compound of the formula (1) in the presence of an effective amount of a catalyst for said isomerization.

10. A process of making a compound of the formula (1)



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

R² is alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)_{n-1}-C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-;

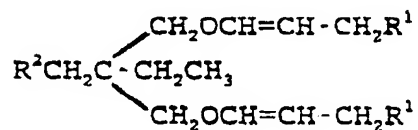
comprising isomerizing an allyl compound of the formula HO-R-(OCH₂CH=CHR¹)_n to a propenyl compound of the formula HO-R-(OCH=CHCH₂R¹) in the presence of an effective amount

of a catalyst for said isomerization, and then replacing the -OH group on said propenyl compound with R².

11. A process according to any one of claims 8-10 wherein R¹ is -H.

12. A process according to any one of claims 8-10 wherein said compound has the formula

10



13. A process according to any one of claims 8-10 wherein said compound has the formula



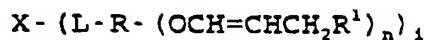
14. A process according to any one of claims 8 to 10 wherein R² is -OCH₃, -OC₄H₉, -OC₈H₁₇, -OC₆H₅, -OC(O)CH₃, -OC(O)CH=CH₂, -OC(O)OC₄H₉, -OC(O)NHC₄H₉ or -OC(O)NH-C₆H₅.

15. A process according to any one of claims 8-10 wherein R¹ is -H and R² is -OC(O)-C₆H₄-C(O)O-R-(OCH=CHCH₃)₂.

16. A product produced by the process of any one of claims 8 to 15.

30

17. A process of making a compound of the formula



5

wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R¹ is -H or -CH₃;

10

wherein X has any of the structures -Ph_{0.1}-C₈H_{2a}-Ph_{0.1}, -Ph_{0.1}-(cyclo-C₅₋₂₀-alkyl)-Ph_{0.1}-, -Ph-Ph-, or -Ph-, wherein Ph is phenylene and a is 1 to 20;

-C_fH_{2f}C(O)C_gH_{2g}-, -C_fH_{2f}OC_gH_{2g}-, -C_fH_{2f}C(O)OC_gH_{2g}-, -C_fH_{2f}PhC_gH_{2g}-, or -C_fH_{2f}C(O)NHC_gH_{2g}-, wherein f and g are each 1 to 12;

15

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-, provided that each R is bonded to an oxygen atom of L, and i is an integer from 1 to 3; or X is -C(O)-, each L is a chemical bond, and i is 1.

20

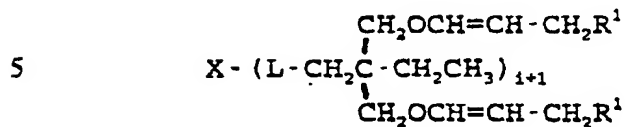
comprising reacting an allyl compound of the formula HO-R-(OCH₂CH=CHR¹)_n with a compound containing a moiety of the formula X-(L-) _{i,1} to form an intermediate of the formula X-(L-R-(OCH₂CH=CHR¹)_n) _{i,1} and then isomerizing said intermediate to said compound of formula (1) in the presence of an effective amount of a catalyst for said isomerization.

25

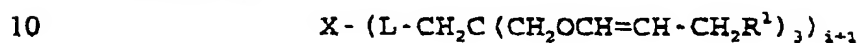
18. A process according to claim 17 wherein R¹ is -H.

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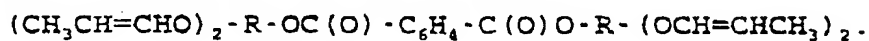
19. A process according to claim 17 wherein said compound has the formula



20. A process according to claim 17 of the formula



21. A process according to claim 17 wherein said compound has the formula



INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 98/17110

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C43/16 C07C43/215 C07C69/12 C07C69/54 C07C69/96
C07C271/12 C07C271/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J.V. CRIVELLO & G. LÖHDEN: "The Preparation of Novel 1-Propenyl Ethers and Their Cationic Photopolymerisation" JOURNAL OF POLYMER SCIENCE: PART A; POLYMER CHEMISTRY, vol. 34, no. 10, 1996, pages 2051-2062, XP002086642 see Scheme 2, p. 2056, compounds 1P-9P	3,9,15, 22,27
A	J.V. CRIVELLO: "Design of network polymers by photopolymerisation" DIE ANGEWANDTE MAKROMOLEKULARE CHEMIE, vol. 240, 1996, pages 83-90, XP002086643 see tables 1,2	3,9,15, 22,27

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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G document member of the same patent family

Date of the actual completion of the international search

3 December 1998

Date of mailing of the international search report

09.12.98

Name and mailing address of the ISA

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Authorized officer

Janus, S

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 98/17110

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1,2,4-8,10-14,16-21,23-26,28-34
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Claims Nos.: 1,2,4-8,10-14,16-21,23-26,28-34

The general formula (1) is too general and encompasses an extremely broad range of totally different compounds, only partly supported by the examples. For instance, a simple compound such as 2-propenyloxyethanol (RN 33813-91-1 and 33813-92-2) falls within the scope of said general formula. Guided by the spirit of the application as supported by specific disclosure of the examples, the search has been limited to trimethylolpropane dipropenyl ether derivatives.

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